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MECHANISTIC ASPECTS OF 1,2-DIALKYLDIMOLYBDENUM (M=M) CHEMISTRY. (U)  
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MECHANISTIC ASPECTS OF 1,2-DIALKYLDIMOLYBDENUM (M=M) CHEMISTRY

by

Malcolm H. Chisholm and Deborah A. Haitko

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Department of Chemistry  
Indiana University  
Bloomington, Indiana 47405

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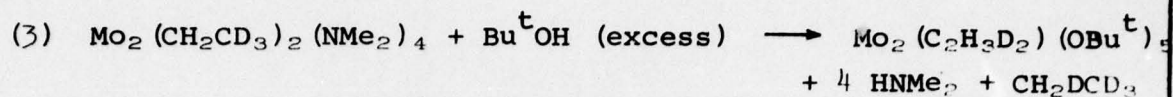
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19. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The following three reactions are reported:  (1) $\text{Mo}_2\text{Cl}_2(\text{NMe}_2)_4 + 2 \text{LiCH}_2\text{CD}_3 \longrightarrow \text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4 + 2 \text{LiCl}$  (2) $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4 + \text{CO}_2 \text{ (excess)} \longrightarrow \text{Mo}_2(\text{O}_2\text{CNMe}_2)_4 + \text{CH}_2=\text{CD}_2 + \text{CH}_2\text{DCD}_3$		



20. continued



The products of these reactions were characterized by  $^1\text{H}$  and  $^2\text{H}$  nmr spectroscopy. The elimination of ethylene and ethane in reaction (2) was found to be intramolecular. The mechanistic conclusions which can be extracted from these findings are noted.

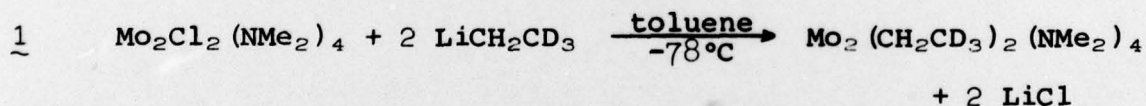
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## Mechanistic Aspects of 1,2-Dialkyldimolybdenum ( $M \equiv M$ ) Chemistry

Sir:

Both historically and commercially  $\sigma$ -alkyl complexes have played a prominent role in the development of mononuclear transition metal chemistry. The recent syntheses and characterizations of 1,2-dialkyl-dimolybdenum and -ditungsten compounds ( $M \equiv M$ ) afford the opportunity of studying the reactivity patterns of  $\sigma$ -alkyl groups bonded to the simplest of metal clusters, namely dimetal centers. We wish here to report the results of labelling studies using the  $\sigma$ - $CH_2CD_3$  ligand and furthermore to address ourselves to the mechanistic implications of these results.

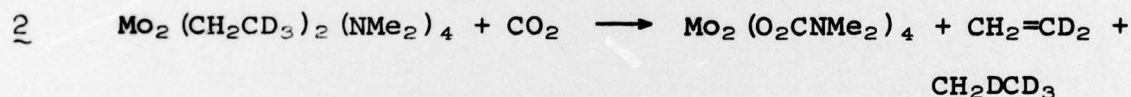
The reaction between  $Mo_2Cl_2(NMe_2)_4$  and  $LiCH_2CD_3$  (2 equiv) proceeded smoothly to yield  $Mo_2(CH_2CD_3)_2(NMe_2)_4$ , according to eq. 1. The 1,2-diethyldimolybdenum compound was purified by



sublimation at  $80^\circ C$ ,  $10^{-6}$  cm Hg. The low temperature limiting  $^1H$  nmr spectra of  $Mo_2(CH_2CD_3)_2(NMe_2)_4$  and  $Mo_2(CH_2CH_3)_2(NMe_2)_4$  obtained at  $-60^\circ C$ , 270 MHz in toluene- $d_8$  are shown in Figures 1a and 1b, respectively. Both compounds exist in a mixture of gauche and anti rotamers with the gauche being the predominant rotamer. The most striking difference is in the ethyl resonances. In the gauche rotamer, which lacks a plane of symmetry, the methylene protons are diastereotopic and at

270 MHz form part of an ABX<sub>3</sub> spectrum. It is therefore obvious from a comparison of the spectra in Figure 1 that the compound Mo<sub>2</sub>(CH<sub>2</sub>CD<sub>3</sub>)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> retains its <sup>2</sup>H label in the methyl position. The methylene protons resemble an AB spin pattern since <sup>2</sup>J<sub>1H-<sup>2</sup>H</sub> is very small compared to the geminal J<sub>1H-<sup>1</sup>H</sub>.

Addition of CO<sub>2</sub> to a hydrocarbon solution of Mo<sub>2</sub>(Et)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> leads to the formation of Mo<sub>2</sub>(O<sub>2</sub>CNMe<sub>2</sub>)<sub>4</sub> (MEM) and equimolar amounts of ethylene and ethane.<sup>4</sup> Reaction 2 was carried out in an nmr tube. The fine yellow precipitate of Mo<sub>2</sub>(O<sub>2</sub>CNMe<sub>2</sub>)<sub>4</sub> was centrifuged to the top of the nmr tube and the <sup>2</sup>H spectrum of the solution was recorded at 220 MHz. The spectrum is shown



in Figure 2a. The <sup>2</sup>H spectrum of CH<sub>2</sub>=CD<sub>2</sub> agreed well with that which can be computed with a knowledge of all the <sup>1</sup>H-<sup>1</sup>H couplings in ethylene<sup>9</sup> and the relative gyromagnetic ratios of <sup>1</sup>H and <sup>2</sup>H.<sup>10</sup>

In order to compare the <sup>2</sup>H spectrum of CH<sub>2</sub>DCD<sub>3</sub> obtained in reaction 2 with that of an authentic sample, we reacted a solid sample of LiCH<sub>2</sub>CD<sub>3</sub> with D<sub>2</sub>O in a vacuum manifold. The gases were condensed into an nmr tube using benzene as solvent and the <sup>2</sup>H spectrum was recorded. This is shown in Figure 2b. The <sup>2</sup>H spectrum of the ethane is identical with that in Figure 2a; furthermore, it is apparent that addition of D<sub>2</sub>O to a solid sample of LiCH<sub>2</sub>CD<sub>3</sub> also induces the formation of

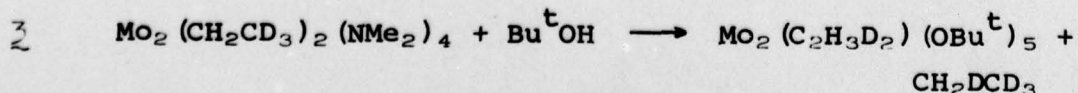


$\text{CH}_2=\text{CD}_2$ .

In a third experiment a mixture of  $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$  and  $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$  was reacted with  $\text{CO}_2$  in a sealed nmr tube and the  $^2\text{H}$  spectrum was recorded: this was identical to that shown in Figure 2a.

The  $^1\text{H}$  spectra of all of the above were also recorded. The  $^1\text{H}$  nmr spectrum of  $\text{CH}_2=\text{CD}_2$  is a complex (AA'XX') but symmetrical spectrum since each proton is coupled to cis and trans  $^2\text{H}$  nuclei,  $I = 1$ , and also to its geminal proton: gem- $\text{J}_{\text{H}-^1\text{H}}$  in ethylene is +2.5 Hz.<sup>9</sup> Significantly, however, the  $^1\text{H}$  nmr spectrum of the ethylene obtained from the addition of  $\text{CO}_2$  to a mixture of  $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$  and  $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$  was merely the superimposition of a single line slightly down-field from the central portion of spectrum obtained for  $\text{CH}_2=\text{CD}_2$ .<sup>11</sup>

Previously we noted<sup>4</sup> that  $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_4$  and  $\text{Mo}_2(\text{Et})_2(\text{NMe}_2)_4$  react with tert-butanol to give  $\text{Mo}_2\text{Me}_2(\text{OBu}^t)_4$  and  $\text{Mo}_2\text{Et}(\text{OBu}^t)_5$ , respectively. In both reactions the replacement of  $\text{NMe}_2$  by  $\text{OBu}^t$  groups with the formation of  $\text{HNMe}_2$  is expected,<sup>12</sup> but in the latter reaction the additional substitution of one ethyl group by  $\text{OBu}^t$  and the liberation of one equivalent of ethane was puzzling to us. Consequently we carried out the reaction of  $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$  with excess  $\text{Bu}^t\text{OH}$  in a sealed nmr tube and recorded the  $^2\text{H}$  spectrum of the products. The reaction proceeds according to equation 3. The ethane is  $\text{CH}_2\text{DCD}_3$  while



the  $\sigma$ -ethyl group has a statistical distribution of deuteriums on the  $\alpha$  and  $\beta$  carbons. The  $^2\text{H}$  spectrum of the  $\sigma$ -ethyl group consists of two broad featureless signals at  $\delta = 2.96$  and 1.72 ppm in the integral ratio 2:3.

These observations allow the following conclusions.

(1) In  $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$   $\beta$ -hydrogen elimination is either kinetically or thermodynamically not favorable. (2) Addition of  $\text{CO}_2$  to  $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$  ( $\text{M}\equiv\text{M}$ ) leads to the formation  $\text{Mo}_2(\text{O}_2\text{CNMe}_2)_4$  ( $\text{M}\equiv\text{M}$ ) by an intramolecular C-H reductive elimination reaction which is preceded by an irreversible  $\beta$ -hydrogen elimination reaction. (3) Addition of  $\text{Bu}^t\text{OH}$  to  $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$  causes the elimination of ethane by a C-H reductive elimination which is also promoted by an irreversible  $\beta$ -hydrogen elimination reaction. The  $\sigma$ -ethyl group subsequently formed in reaction 3 is formed from  $\text{CH}_2=\text{CD}_2$  and a hydroxyl hydrogen atom from  $\text{Bu}^t\text{OH}$  (or possibly, but less likely the amine hydrogen of  $\text{HNMe}_2$ ).  $\beta$ -hydrogen elimination from the  $\sigma$ -ethyl ligand is then a reversible process with the equilibrium favoring the  $\sigma$ -ethyl group.

These results raise many interesting mechanistic questions concerning factors favoring  $\beta$ -hydrogen elimination and reductive elimination reactions in dinuclear chemistry. We resist the temptation to speculate at this time but do note that our observations have one parallel with mononuclear transition metal chemistry. Reductive elimination involving C-H bond formation is more facile than reductive elimination involving



C-C bond formation.

Malcolm H. Chisholm\* and Deborah A. Haitko  
Department of Chemistry  
Indiana University  
Bloomington, Indiana 47405

Acknowledgement

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## References and Footnotes

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10.  $\gamma_{\text{H}} = 2.675 \times 10^4$  radians/sec. gauss.  
 $\gamma_{\text{D}} = 4.107 \times 10^3$  radians/sec. gauss.
11. This isotope influence on the chemical shift of the ethylenic protons is really only apparent in nmr spectra obtained at high field, 220 MHz in this instance.

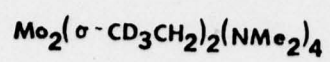
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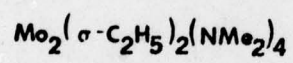
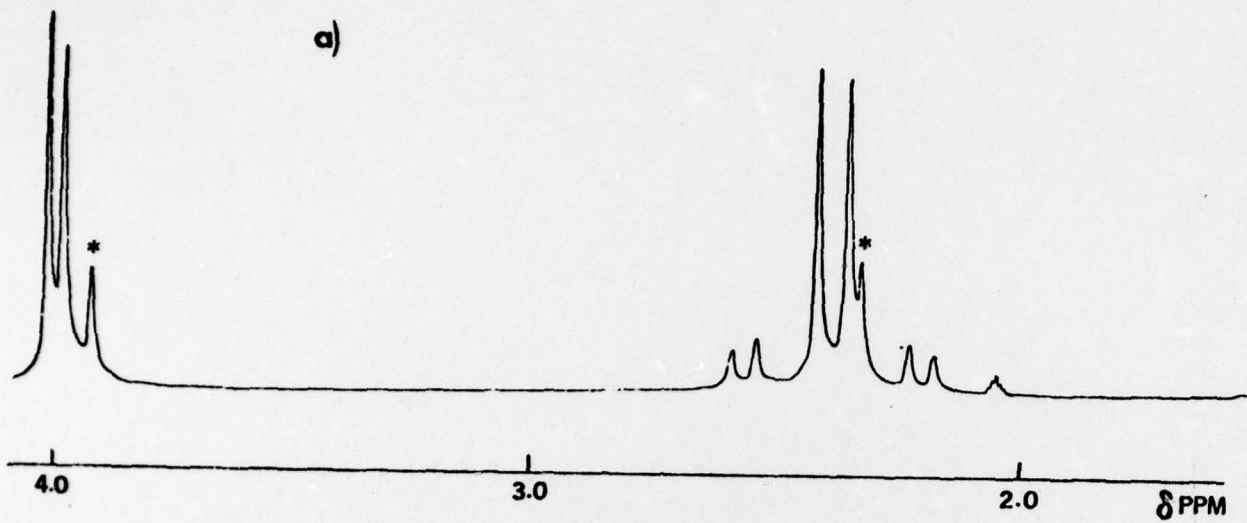
Captions to Figures

Figure 1. Proton NMR spectra recorded at 270 MHz,  $-61^{\circ}\text{C}$  in toluene- $\text{d}_8$  of a) \*-anti and gauche -  $\text{Mo}_2(\text{CH}_2\text{CD}_3)_2(\text{NMe}_2)_4$  and b) \*-anti and gauche -  $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$ . c) \*\* represents residual protonated toluene.

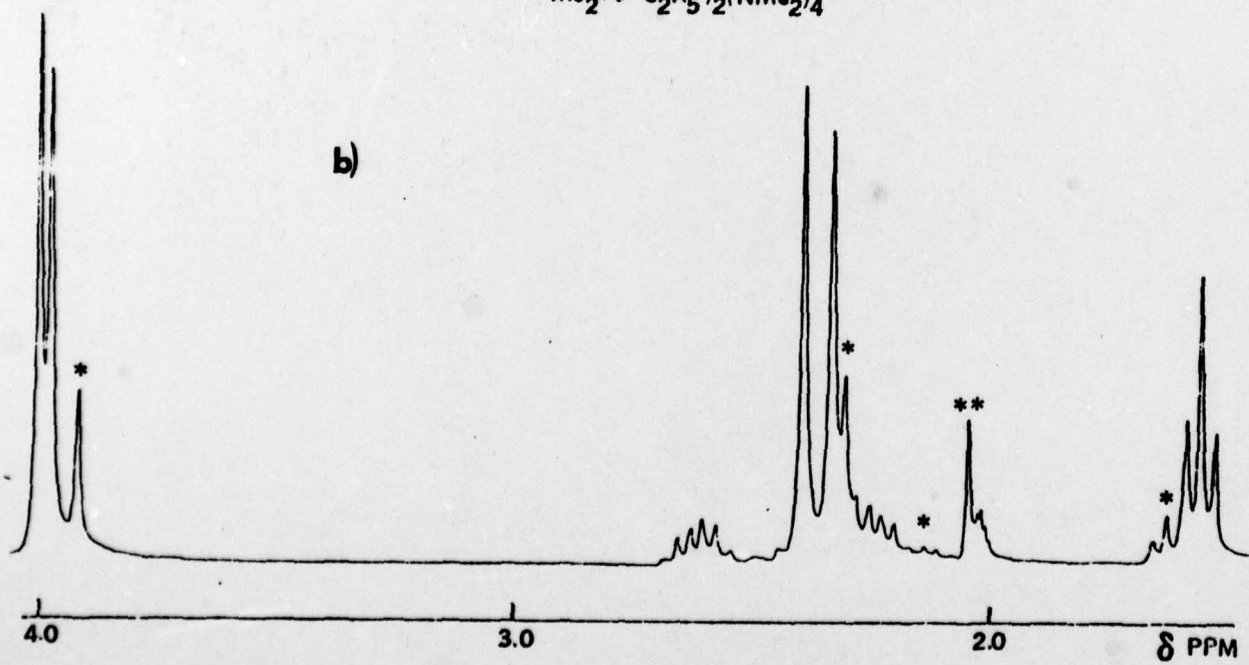
Figure 2. Deuterium NMR spectra recorded at  $16^{\circ}\text{C}$  and 220 MHz of the gases formed in the reactions of a)  $\text{CO}_2$  with  $\text{Mo}_2(\text{CH}_2\text{CH}_3)_2(\text{NMe}_2)_4$  and b)  $\text{D}_2\text{O}$  with  $\text{LiCH}_2\text{CD}_3$ . Both spectra were recorded in benzene.



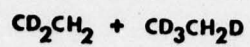
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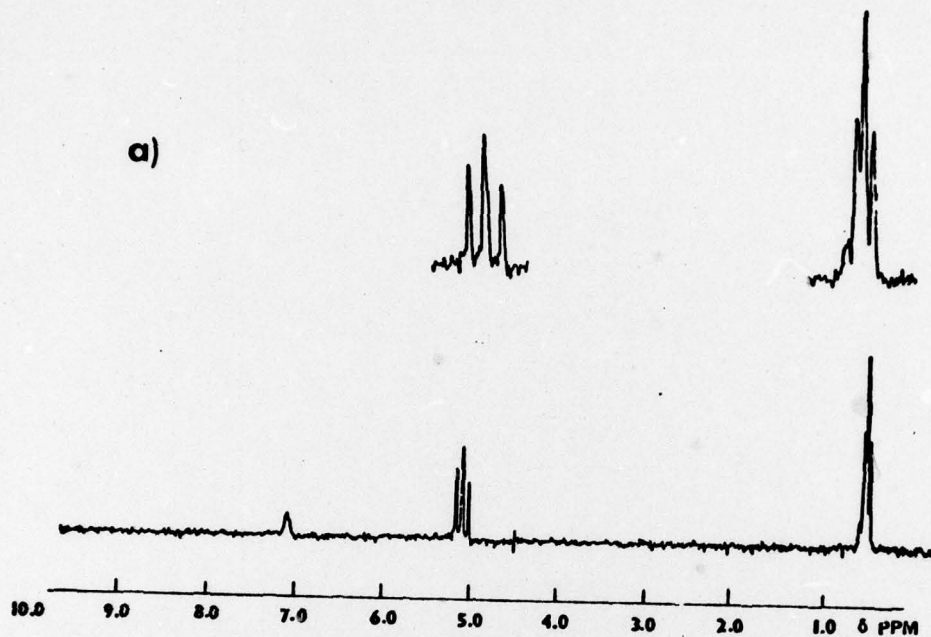
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$^2\text{H}$



a)



b)

